Photophysical Properties and Photochemistry of Substituted Cinnamates for UVB Blocking: Effect of Hydroxy, Nitro, and Fluoro Substitutions at *ortho*, *meta*, and *para* Positions

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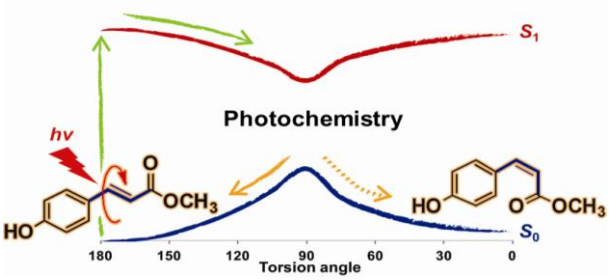
Cinnamate derivatives, an important class of organic UV filters, are widely used as ultraviolet B (UVB) blocking compounds in cosmetic sunscreens. The photophysical properties and photochemistry of various substituted cinnamates have been investigated theoretically. This series includes monohydroxy-, -nitro, and -fluoro derivatives at the *ortho*, *meta*, and *para* positions. The absorption spectra of these compounds were satisfactorily reproduced by the direct symmetry-adapted cluster-configuration interaction (SAC-CI) method with the experimental absorption bands. The transition character of the low-lying two ππ* and σπ* states for these 9 derivatives were analyzed in detail. The *para* derivatives have a different transition character of the ππ* transitions compared with those of the *ortho* and *meta* derivatives. To evaluate the UVB blocking of these derivatives, the calculated radiative lifetimes indicate that the *ortho*- and *meta*-substituted derivatives have longer lifetimes for emission than the *para* derivatives. The potential energy curves of the ground (S_0) and excited (S_1) states of the hydroxy derivatives were examined to investigate *cis–trans* photoisomerization. The *ortho* and *meta* derivatives have an energy barrier to the conical intersection resulting in fluorescence, whereas *para* derivatives show nonradiative decay because they have no energy barrier. The hydroxy derivatives were found to be excellent UV absorbers because of their broad absorption in both the UVA and UVB regions as well as their higher photostability. The present work provides important information for the design of UVB blocking compounds and for the possibility of photoactive molecules in the UV–Vis wavelength domain.



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